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(54) Method of improving scuff and cut resistance of ionomer covered game ball

(57) A game ball has an ionomeric cover 12 which comprises a combination of ionomeric crosslinks and covalent crosslinks. The game ball cover is superior in at least one of cut resistance and scuff resistance to a conventional cover that does not have covalent crosslinks but is otherwise substantially identical in composition. The game ball cover is particularly useful for improving the durability of golf balls to be struck with sharp-grooved clubs. The crosslinking may comprise radiation-induced crosslinking.

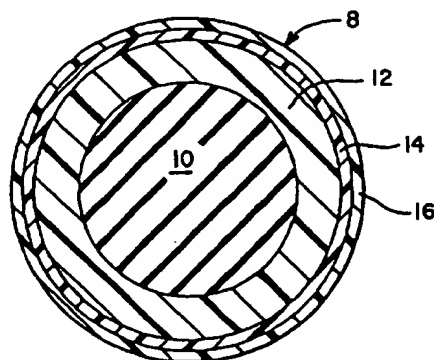


FIG. 1

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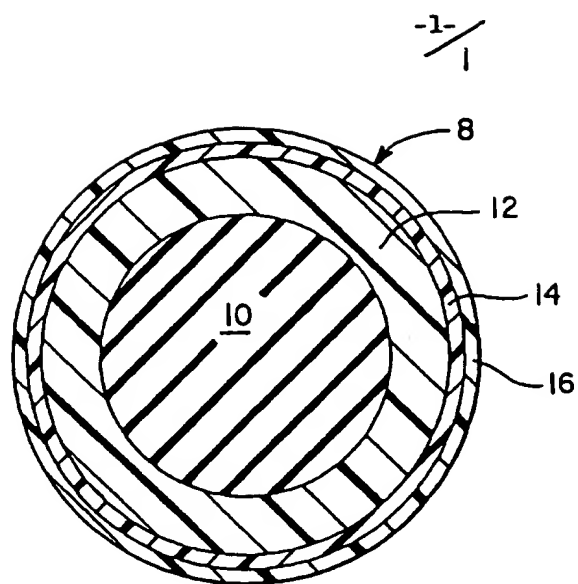


FIG. 1

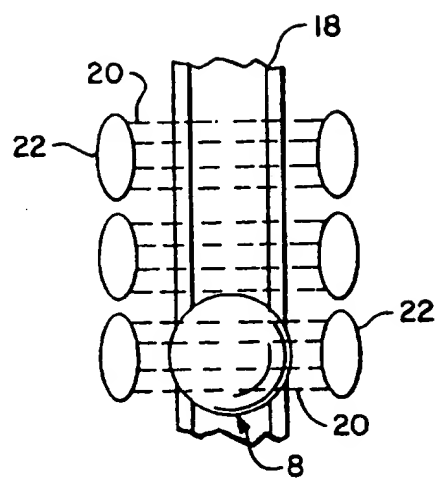


FIG. 2

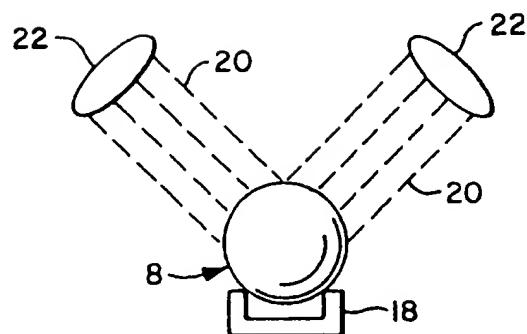


FIG. 3

METHOD OF IMPROVING SCUFF AND CUT RESISTANCE OF IONOMER
COVERED GAME BALL

This invention relates generally to balls, and
5 more particularly to a game ball having an ionomeric
cover, for example a golf ball.

Before the development of ionomers, balata was
the preferred material for golf ball covers.
Polyethylene also was proposed for use as a golf ball
10 cover material but was generally deemed highly inferior
to balata in imparting playability and durability
characteristics to the ball, due to its brittleness and
high hardness, and thus never became a commercially
successful golf ball cover material.

15 Balata golf ball covers have now been replaced
to a great extent by ionomeric cover materials.
Ionomers may be copolymers of an olefin and an α , β -
ethylenically unsaturated carboxylic acid with a portion
of the carboxylic acid groups neutralized by a metal
20 ion. The metal ions serve as crosslinking agents,
because they are ionically bonded to carboxylic acid
groups in adjacent copolymer chains. Instead of having
thermally irreversible covalent bonding, ionomers have
thermolabile crosslinking in which metal ions become
25 part of the chemical structure of the ionomer upon

crosslinking, and these crosslinks are reversible. For purposes of the present application, this type of crosslinking is referred to as ionic crosslinking. One of the advantages of ionic crosslinking in golf ball materials is the ability of ionic bonds to re-form after breaking as a result of processing at elevated temperatures.

There are numerous advantages to the use of ionomers in making golf ball covers. On the other hand, one drawback of conventional golf balls with soft ionomeric covers is that the covers are prone to scuffing and cutting, particularly when hit with irons which have sharp grooves. It would be useful to develop a golf ball with a soft ionomeric cover which is highly resistant to cutting and scuffing by sharp-grooved clubs.

Some examples of the present invention are mentioned below.

One object of the invention is to provide an ionomeric game ball cover having improved scuff resistance and/or cut resistance.

Another object of the invention is to provide a method for imparting improved scuff resistance and/or cut resistance to a game ball cover.

degree of covalent crosslinking may be sufficient to impart to the cover a Shore D hardness at most 5.0% greater than the Shore D hardness of a cover having a substantially identical composition but which does not have a substantial degree of said covalent crosslinking. Said degree of covalent crosslinking may be sufficient to impart to the ball a PGA compression at least 5% harder than the PGA compression of a ball with a cover having a substantially identical composition but which does not have a substantial degree of covalent crosslinking. Said degree of covalent crosslinking may be sufficient to impart to the ball a coefficient of restitution at least 0.50% greater than a coefficient of restitution of a ball with a cover having a substantially identical composition but which does not have radiation-induced covalent crosslinking. Said copolymer may have radiation-induced covalent crosslinking to increase the resistance of the cover to at least one of scuffing and cutting. Said radiation-induced covalent crosslinking may be provided by irradiating the cover by a method comprising utilising an electron beam. Said irradiation may comprise electron beam dosage of at least 1 megarads.

Said irradiation may be before and/or after
25 application of coating over the cover. After said

irradiation, a top coating may be applied to the irradiated cover. Said copolymer may further comprise acrylate. Said neutralization of said carboxylic acid may correspond to 10 to 100% neutralization with
5 said metal ions. Said cover may have a Shore D hardness of at most 65.

A second aspect of the present invention provides a method of forming a ball of said first aspect of the present invention.

10 The invention in one preferred form is a game ball having a cover comprising an ionomer resin. The ionomer resin may comprise a copolymer of an olefin and an α , β -ethylenically unsaturated carboxylic acid which is 10-100% neutralized with metal ions. The copolymer
15 has a sufficient degree of covalent crosslinking to impart to the cover improved resistance to at least one of scuffing and cutting. In a particularly preferred form of the invention, the game ball is a golf ball. Preferably, the game ball has a dimpled surface. The
20 covalent crosslinking preferably comprises irradiation-induced covalent crosslinking.

In another form of the invention, the degree of covalent crosslinking is appropriate to impart to the cover a Shore D hardness which is no more than 10%
25 greater, and more preferably no more than 5% greater,

than the Shore D hardness of a cover having an identical composition but which does not comprise a substantial degree of covalent crosslinking. Preferably, the copolymer further comprises acrylate.

5 Another aspect of the invention is a method of forming a game ball having a cover comprising an ionomer, said method comprising irradiating the ionomer in the cover under conditions appropriate to covalently crosslink the ionomer in order to increase the
10 resistance of the cover to at least one of scuffing and cutting without substantially impairing other playability characteristics of the ball.

 In a particularly preferred form of the invention, the game ball is a golf ball. Preferably,
15 the game ball has a dimpled surface.

 In one preferred form of said method of the invention, a game ball is subjected to irradiation comprising electron beam treatment at a dosage of at least 1 megarads. The game ball cover preferably is
20 irradiated prior to application of a top coat over a cover. The method of the invention preferably further comprises the step of applying a top coat over the cover before or after irradiation.

 The present invention is exemplified by the
25 following detailed disclosure with reference to the

accompanying drawings wherein:

Fig. 1 shows one example of a golf ball according to the present invention.

Figs. 2 and 3 schematically show one example for practicing the method of the present invention.

The game balls of the present invention are surprisingly superior in their scuff (abrasion) resistance and cut resistance to conventional game balls which have not been electron beam treated, and which contain similar quantities of ionomer and have a similar hardness. Furthermore, the golf balls and other game balls of the invention are comparable in scuff and cut resistance to game balls having non-ionomeric compositions, such as polyurethanes, with similar properties of compression, coefficient of restitution (COR), and hardness.

The game balls of the present invention may be formed by first obtaining an uncoated or coated game ball having an ionomeric cover. An "uncoated" game ball as the term is used in this application is a one, two, or multi-piece game ball to which no primer or top coat has been applied over the ionomeric cover. In contrast, a "coated" game ball as this term is used in this application is a ball which has a primer coat and/or a top coat over the ionomeric cover layer. The coated or

uncoated game ball of the invention may be subjected to irradiation under conditions appropriate to induce covalent crosslinking of the ionomer. This type of direct covalent bonding has been found to take place in
5 ionomeric cover materials when electron beam treatment is applied at a dosage of 2 or more megarads and is expected to also be useful at lower dosages, for example, 1 megarad.

For clarity of description and ease of
10 understanding, the invention will be described in connection with golf balls although it will be understood that other game balls, for example softballs, basketballs, baseballs, soccer balls, volleyballs, street hockey balls, footballs, etc. can advantageously employ
15 the features of the present invention.

Referring now to the drawings, and in particular to Fig. 1, one example of a golf ball according to the present invention is shown and is designated as 8. The ball has a core 10, which is
20 solid, or is formed from any other suitable type of core composition. An ionomeric cover 12 surrounds the core 10. A thin primer coat 14 is applied to the outer surface of cover 12. A thin top coat 16 surrounds the primer coat 14. The thicknesses of primer coat 14 and
25 top coat 16 are exaggerated for illustrative purposes.

of in the range of 40 - 100 after irradiation. It has been found that excellent results are obtained when the post-irradiation PGA compression of the golf balls is in the range of 60 - 100. The irradiation preferably
5 results in an increase in PGA compression of at least 5% compared to the PGA compression of the ball prior to treatment. The coefficient of restitution of the golf balls of the invention after treatment may be in the range of .780 or greater. Preferably, the COR of the
10 golf balls is in the range of .790 - .830 and most preferably in the range of .800 - .830. The Shore D hardness of the golf balls of the invention after irradiation may be in the range of 40 - 80. Particularly good results are obtained when the Shore D
15 hardness of the golf balls is in the range of 50 - 70, and most preferably in the range of 50 - 60.

The invention is particularly well suited for use in making dimpled, pebbled, and other game balls which do not have a smooth outer surface, for example
20 game balls with simulated stitching. A smooth ball is less susceptible to scuffing than a dimpled ball since dimples give the golf club groove a sharp-edged surface to "catch." Pebbles clearly are susceptible to shearing when dribbled on a hard surface, or the like. Likewise
25 on a molded-cover softball, the stitching is a raised

4 Material removed or barely
attached

Cut resistance was measured in accordance with the following procedure: a golf ball was fired at 41.148 meters per second (135 feet per second) against the leading edge of a 1994 Top-Flite Tour pitching wedge, wherein the leading edge radius is 0.079 cm (1/32 inch), the loft angle is 51 degrees, the sole radius is 6.35 cm (2.5 inches), and the bounce angle is 7 degrees.

10 The cut resistance of the balls tested herein
was evaluated on a scale of 1 -5. A 5 represents a cut
that extends completely through the cover to the core; a
4 represents a cut that does not extend completely
through the cover but that does break the surface; a 3
15 · does not break the surface of the cover but does leave a
permanent dent; a 2 leaves only a slight crease which is
permanent but not as severe as 3; and a 1 represents
virtually no visible indentation or damage of any sort.

It has been found that golf balls which are
20 treated according to the irradiation technique of the
present invention exhibit a particular improvement in
scuff and/or cut resistance. This improvement is
particularly significant when the golf balls are struck
with a square-grooved iron. It has been found that
25 square-grooved irons and other sharp-grooved irons tend

to abrade and damage golf ball covers more readily than
irons having "V-type" grooves.

Having generally described the invention, the
following detailed examples are included for purposes of
5 illustration so that the invention may be more readily
understood and are in no way intended to limit the scope
of the invention unless otherwise specifically
indicated.

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Example 1

Polybutadiene golf ball cores having an average coefficient of restitution (COR) of .790 and a
5 PGA compression of 90 were obtained. The cores were covered with a relatively soft, 0.1397 cm (0.055 inch) thick cover formed from an ionomeric composition, designated as ionomer 1, which comprises a blend of a hard sodium ionomer and a soft zinc ionomer. Pigments
10 and an optical brightener were also included in the cover composition. The hard ionomer is a copolymer containing two monomer types, namely an α -olefin and an acrylic-type carboxylic acid. The soft ionomer is a copolymer which contains three types of monomers,
15 an α -olefin, an acrylic-type carboxylic acid, and an acrylate. The cover was formed over the core. The balls were primed with a polyurethane-based primer with a thickness of 0.0127 cm (0.5 thousandths of an inch) and coated with a polyurethane top coat with a thickness
20 of 0.0127 cm (0.5 thousandths of an inch). The properties of these balls prior to electron beam treatment are shown in Table 1.

A portion of the balls were subjected to electron beam treatment at dosages of 2,4,6,8, and 11
25 megarads at an energy level of 10 MeV. Changes in the properties of the balls are shown in Table 1.

As indicated in Table 1, the scuff resistance of the golf balls substantially improved in the range of electron beam dosages of 2 to 6 megarads. The cut resistance of the balls improved in the range of electron beam dosages of 6 to 8 megarads. Meanwhile, the change in Shore D hardness in the dosage range of 2 to 8 was only 1.

TABLE 1

	<u>Cover</u> <u>Material</u>	<u>Dosage</u> <u>(Megarads)</u>	<u>Weight</u>	<u>PGA</u> <u>Comp</u>	<u>COR</u>	<u>Shore D</u>	<u>Scuff</u> <u>Resistance</u>	<u>Cut</u> <u>Resistance</u>
10	Ionomer Blend 1	2.0	45.6	93	.788	54	2.5	2 - 3
	(coated prior to	4.0	45.6	97	.797	55	1.2	2 - 3
	treatment)	6.0	45.6	98	.795	55	1.5	2 - 3
15		8.0	45.6	98	.797	55	1.5	2
		11.0	45.6	101	.802	55	1.5	2
		0	45.6	92	.787	54	3.5	3
	Ionomer Blend 2	2.0	45.4	96	.822	63	--	--
	(uncoated)	4.0	45.4	97	.822	63	--	--
20		0	45.4	88	.812	62	--	--
	Ionomer Blend 2	6.0	45.6	101	.829	64	1.5	1 - 2
	(coated with	8.0	45.6	103	.828	64	1.5	1 - 2
	primer and top	0	45.6	88	.813	63	2.0	1 - 2
25	coat prior to							
	treatment)							

(Weight = Ball weight, grams)

Example 2

Golf ball cores having an average PGA compression of 85 and an average COR of .800 were
5 obtained. The cores were covered with a hard zinc-sodium ionomeric composition containing two monomer types, namely an α -olefin and a carboxylic acid. The initial properties of the covered cores prior to priming and finish coating are shown in Table 1.

10 A portion of the golf balls were painted with the same polyurethane-based primer as was used in Example 1 and then coated with the same polyurethane top coat as was used in Example 1. Subsequently, a portion of both the unprimed and unfinished golf balls and the
15 primed and finished golf balls were subjected to electron beam treatment in the dosages shown in Table 1. Properties of compression, COR, Shore D hardness and scuff resistance are shown in Table 1.

As indicated in Table 1, the scuff resistance
20 of the finished golf balls increased substantially while resulting in a minimal increase in Shore D hardness.

In this specification (description, claims and abstract), precise values include values about or substantially the same as precise values, e.g. 10%
25 includes values about or substantially the same as 10%.

10. A ball as claimed in claim 9, wherein said radiation-induced covalent crosslinking has been provided by irradiating the cover by a method comprising utilising an electron beam.

5

11. A ball as claimed in claim 10, wherein said irradiation is at least 1 megarads.

12. A ball as claimed in claim 11, wherein said
10 irradiation is at least 2 megarads.

13. A ball as claimed in 12, wherein said irradiation is in the range 2 to 12 megarads.

15 14. A ball as claimed in claim 13, wherein said irradiation is in the range 2 to 6 megarads.

15. A ball as claimed in claim 13, wherein said irradiation is in the range 4 to 8 megarads.

20

16. A ball as claimed in claim 13, wherein said irradiation is in the range 6 to 8 megarads.

17. A ball as claimed in any one of claims 9 to
25 16, wherein the irradiation has an intensity in the range of 1 to 20 MeV.

18. A ball as claimed in any one of claims 9 to 17, wherein said irradiation was applied before and / or after application of at least one coating over the cover.

5

19. A ball as claimed in any one of claims 9 to 18, wherein after said irradiation top coating was applied to the irradiation cover.

10 20. A ball as claimed in any one of claims 1 to 19, wherein said copolymer further comprises acrylate.

15 21. A ball as claimed in any one of claims 1 to 20, wherein said neutralization of said carboxylic acid corresponds to 10 to 100% neutralization with said metal ions.

22. A ball as claimed in any one of claims 1 to 20 21, wherein the cover has a Shore D hardness of at most 65.

23. A ball as claimed in claim 1, substantially as hereinbefore described with reference to the 25 accompanying drawings.

24. A ball as claimed in claim 1, substantially as described in the Examples.

25. A game ball having a cover comprising an ionomer resin, the ionomer resin comprising copolymer of olefin and α , β -ethylenically unsaturated carboxylic acid which is 10 - 100% neutralized
5 with metal ions, the copolymer having a sufficient degree of covalent crosslinking to impart to the cover improved resistance to at least one of scuffing and cutting.

10 26. A game ball according to claim 25, wherein the game ball is a golf ball.

27. A game ball according to claim 25, wherein the cover has a dimpled surface.

15

28. A game ball according to claim 25, wherein the covalent crosslinking comprises radiation-induced covalent crosslinking.

20 29. A game ball according to claim 25, wherein the degree of covalent crosslinking is appropriate to impart to the cover a Shore D hardness which is no more than 10% greater than the Shore D hardness of a cover having a substantially identical composition but which does not
25 include a substantial degree of covalent crosslinking.

30. A game ball according to claim 25, wherein the copolymer further comprises an acrylate.

31. A game ball according to claim 25, wherein the cover has a Shore D hardness of 65 or less.

32. A game ball according to claim 28, wherein the degree of covalent crosslinking is sufficient to impart to the ball a coefficient of restitution which is at least 0.50% greater than a coefficient of restitution of a ball with a cover having a substantially identical composition but which does not have radiation-induced covalent crosslinking.

33. A game ball according to claim 26, wherein the degree of covalent crosslinking is sufficient to impart to the ball a PGA compression which is at least 5% harder than the PGA compression of a golf ball with a cover having a substantially identical composition but which does not have a substantial degree of covalent crosslinking.

34. A game ball having a cover comprising ionomer resin, the ionomer resin comprising copolymer of α -olefin, acrylate, and α,β -ethylenically unsaturated carboxylic acid which is 10 - 100% neutralized with metal ions, the copolymer having a degree of radiation induced covalent crosslinking which is sufficient to substantially improve the resistance of the cover to a least one of scuffing and cutting while resulting in a cover hardness (Shore D) which is no more

than 5.0% higher than the Shore D hardness of a cover which is substantially identical in composition but does not contain covalent crosslinking.

5 35. A game ball according to claim 34, wherein the game ball is a golf ball.

36. A game ball according to claim 34, wherein the cover has a dimpled surface.

10

37. A method of forming a ball optionally a game ball, comprising:

obtaining a game ball having a cover comprising an ionomer;

15 and

irradiating the ionomer in the cover under conditions appropriate to covalently crosslink the ionomer in order to increase the resistance of the cover to at least one of scuffing and cutting without substantially impairing

20 other playability characteristics of the ball.

38. A method according to claim 37, wherein the game ball is a golf ball.

25 39. A method according to claim 37, wherein the game ball has a dimpled surface.

40. A method according to claim 37, wherein the cover is irradiated using an electron beam.

41. A method according to claim 40, wherein the
5 cover is subjected to electron beam treatment at a dosage of at least 2 megarads.

42. A method according to claim 37, wherein the game ball cover is irradiated after application of a
10 coating over the cover.

43. A method according to claim 37, comprising the step of applying a top coating over the cover after irradiation.

15

44. A method according to claim 37, wherein the ionomer comprises copolymer of α -olefin, acrylate, and α,β -ethylenically unsaturated carboxylic acid which is 10 - 100% neutralized with
20 metal ions.

45. A method of forming a game ball, comprising:
obtaining an unfinished game ball having a cover comprising an ionomer;
25 forming a coating over the cover; and
irradiating the ionomer in the cover at a dosage of at

least 2 megarads to covalently crosslink the ionomer to a degree sufficient to increase at least one of the scuff resistance and cut resistance of the cover without reducing the coefficient of restitution of the cover.

5

46. A method according to claim 45, wherein the game ball is a golf ball.

47. A method according to claim 45, wherein the
10 game ball has a dimpled surface.

48. A method according to claim 45, wherein the ionomer comprises copolymer of α -olefin, acrylate, and α,β -ethylenically unsaturated
15 carboxylic acid which is 10 - 100% neutralized with metal ions.

49. A method of forming a golf ball according to claim 1, said method being substantially as hereinbefore
20 described with reference to the accompanying drawings.

50. A method of forming a golf ball according to claim 1, substantially as described in the Examples.



The
Patent
Office

30.

Application No: GB 9702144.8
Claims searched: 1-50

Examiner: Alan Kerry
Date of search: 25 April 1997

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK CI (Ed.O): C3J JAC, JCH; C3P PFE; C3V VEM

Int CI (Ed.6): A63B 37/12; C08F 8/44, 122/02; C08J 3/28

Other: Online databases: WPI, CLAIMS

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	WPI Abstract Accession Number 88-060404/09 & JP 63 015832	1-3, 25, 37 at least

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.